CATALYTIC GASIFICATION OF SHALE OIL

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INTRODUCTION

Although the United States has large proven reserves of natural gas, our annual marketed production increased from less than 4 trillion cubic feet in 1945 to nearly 16 trillion cubic feet in 1964 (9). This increase, coupled with our decreasing ratio of reserves to production, has stimulated interest in possible methods for supplementing our future natural gas supply. The large quantities of oil shale in the western United States suggest the use of oil shale or shale oil for such supplemental purposes. Various authors have reported on the thermal gasification of these materials (5,6,7,8). The present study is concerned with catalytic hydrogasification of crude shale oil, using as catalysts depleted uranium and cobalt molybdate on alumina supports.

Previous experiments in catalytic hydrogenation of crude shale oil at the Laramie Petroleum Research Center of the Bureau of Mines (3,4) showed that pressures in excess of 2,000 pounds per square inch greatly suppressed the formation of methane, ethane, and catalyst deposits. At 500 pounds pressure, catalyst deposits became excessive. The gasification experiments were, therefore, made at 1,000 pounds pressure as a means of obtaining high gas yields with moderate catalyst deposits.

APPARATUS AND PROCEDURE

A simplified flow diagram of the apparatus used for the gasification study is shown in figure 1. The reactor was a vertical 2-9/16-inch-I.D. by 32-inch-long stainless steel vessel; it was modified for these experiments by a stainless steel sleeve that was inserted to reduce the internal diameter to 1 inch. This modification effected improved temperature control. The reactor contained 18 inches of alundum granules at the top to serve as a preheater, 12-1/2 inches of catalyst, and 1-1/2 inches of alundum granules at the bottom. Catalyst temperatures were determined by five thermocouples spaced at 2-1/4-inch intervals in a central thermowell in the catalyst bed.

Hydrogen and oil were mixed at the inlet to the reactor and passed downward through the catalyst. Liquid products were separated in two high-pressure separators operated in series at $350\,^{\circ}\text{F}$. and $40\,^{\circ}\text{F}$. Gas from the cold receiver was metered and stored until it could be sampled for mass spectrometer analysis.

Each gasification experiment was run for 6 hours with 12,000 cubic feet of hydrogen per barrel. At the end of an experiment, liquid products were distilled into a light-ends fraction collected in a dry-ice trap, a naphtha fraction boiling up to 400°F., and a recycle fraction containing everything boiling above 400°F. The light ends from the cold trap were analyzed by the mass spectrometer and appropriate weights were added to the gaseous and liquid products. Carbon deposits in the reactor were determined by measuring the carbon dioxide obtained when passing air through the reactor to regenerate the catalyst.

CATALYSTS

The catalysts used were commercial cobalt molybdate and a laboratory-prepared depleted uranium catalyst. The cobalt molybdate is a rugged catalyst, able to stand repeated regenerations and exposure to high temperatures such as those used in gasification work. It consisted of cobalt and molybdenum oxides on 6- to 8-mesh alumina

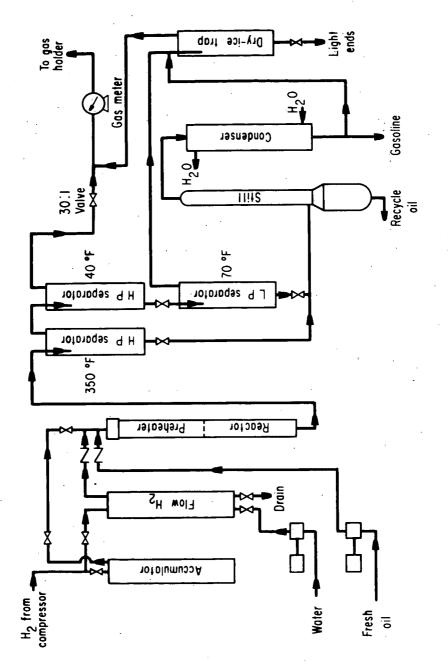


FIGURE 1-Hydrogenation unit

granules. The uranium catalyst consisted of 7.7 percent depleted uranium (uranium from which the U-235 has been removed) in the oxide form on 1/8-inch H-151 alumina balls. This catalyst had produced high gas yields in previous hydrogenation experiments with shale oil at the Laramie Petroleum Research Center, and these results suggested its possible use as a hydrogasification catalyst. Both catalysts were maintained under a hydrogen atmosphere at approximate reaction temperature and pressure for about 12 hours before each experiment.

PEEDSTOCK

The crude shale oil used for these studies was prepared in the Bureau of Mines gas-combustion retort at Rifle, Colorado. It was filtered before use to reduce the ash content to a few hundredths of 1 percent. Properties are shown in table 1. The

TABLE 1. - Properties of crude shale oil

Specific gravity at 60°/60°F.		0.9408
Elemental analysis:		•
Sulfur	wt. %	0.68
Nitrogen	wt. %	2.18
Carbon	wt. %	83.96
Oxygen (by diff.)	wt. %	11.40
Hydrogen/carbon atomic ratio		1.61
Carbon residue	wt. %	3.5
Iron	p.p.m.	40
Zinc and arsenic	• •	Present
Viscosity at 140°F.	cs.	28.30
Viscosity at 210°F.	cs.	8.23
ASTM gas-oil dist'n at 760 mm.:		
I.B.P.	°F.	407
Max. (cracking)	°F.	695
Recovery	vol. %	37.5
Residue	vol. %	62.5

oil contains a large amount of sulfur-, nitrogen-, and oxygen-containing compounds, and more than half of it may consist of non-hydrocarbons (2). It has a high viscosity and contains no gasoline-boiling-range material. The hydrogen-carbon mole ratio of 1.61 shows that additional hydrogen must be added to the oil in order to convert it to pipeline gas.

CALCULATIONS

All gas measurements are reported at $60\,^{\circ}\mathrm{F}$. and 760 mm. mercury pressure. The hydrogen feed rate of 12,000 cubic feet per barrel at these conditions was 1.1 times the stoichiometric amount of about 10,890 cubic feet needed to convert the crude oil completely to methane, hydrogen sulfide, ammonia, and water. The yield of methane as percent of stoichiometric was calculated by dividing the volume in cubic feet per barrel by 8,740, which was the stoichiometric yield at the given conditions.

Conversion of feedstock was defined to be that portion of the feed converted to materials other than liquid oil and gas heavier than propane. It would include water, hydrogen sulfide, ammonia, coke, and gas. Weight percent conversion was defined as 100 minus the weight percent liquid and gaseous products heavier than propane. Yields of methane as percent of conversion were obtained by dividing the weight percent methane by the weight percent conversion and multiplying by 100.

Gross heating values were calculated from component heating values used by the Bureau of Mines in reporting the analyses of natural gases (1). The values were calculated at 760 mm. mercury pressure to agree with the volume measurements.

RESULTS WITH DEPLETED URANIUM CATALYST

Table 2 shows the results from five experiments in hydrogasifying crude shale oil over depleted uranium catalyst at a space velocity of 0.5 volumes of oil per volume of catalyst per hour. Average reaction temperatures for the different experiments were from 880° to $1,102^{\circ}F$.

Total gas volumes increased from 762 cubic feet per barrel at 880° F. to 3,303 cubic feet at $1,102^{\circ}$ F.; at the same time, the methane content of the gas increased from 47.9 to 53.5 volume percent, resulting in a change in the volume of methane from 365 to 1,767 cubic feet. A corresponding decrease in the heating values of the gas occurred, from 1,589 to 1,481 Btu per cubic foot, as the heating values tended to approach that of methane.

Expressed on the weight basis, the yield of methane increased from 4.7 percent at 880° F. to 22.6 percent at $1,102^{\circ}$ F., and total conversion increased from 23.6 to 69.4 percent; the corresponding change in methane yield expressed as weight percent of conversion was from 19.9 to 32.6 percent.

RESULTS WITH COBALT MOLYBDATE CATALYST

Table 3 shows results from hydrogasifying crude shale oil over cobalt molybdate catalyst at a space velocity of 1.0 volume of oil per volume of catalyst per hour. The average reaction temperatures from 974° to 1,183°F, were higher than those used with depleted uranium catalyst. Consequently, greater gas yields were obtained with the cobalt molybdate. However, similar trends were shown by the results obtained with both catalysts.

Conversion increased from 34.1 to 85.1 percent as the average temperature was increased from 974° to $1,183^{\circ}$ F., and, at the same time, methane yield, as weight percent of conversion, increased from 24.6 to 46.6 percent. Also, the methane content of the gas increased from 45.8 to 63.0 volume percent. The increased percentage of methane in the gas at the higher temperature and conversion levels was reflected in the heat content of the gas, which decreased from 1,601 Btu per cubic foot for the gas obtained at 974° F. to 1,315 Btu per cubic foot for the gas obtained at $1,183^{\circ}$ F.

Table 4 shows results from hydrogasifying crude shale oil over cobalt molybdate at space velocities of 0.50 and 0.25. Results of two experiments at different temperatures are shown for each space velocity.

Decreasing the space velocity had much the same effect as increasing the reaction temperature. Comparing results obtained at 1,106°F. average temperature and 0.25 space velocity with those obtained at 1,114°F. and 0.50 space velocity shows that greater methane yield, greater total gas yield, greater conversion, and higher methane yields expressed either as percent of conversion or percent of total gas were obtained at the lower space velocity. Heating value of the gas is lower for the gas produced at the lower space velocity because of the higher methane content. These comparisons can be extended to the results shown in table 3 for the experiment at 1,106°F. and 1.0 space velocity.

The highest methane yield, of 4,341 cubic feet per barrel, and highest gas yield, of 5,725 cubic feet per barrel, were obtained at the highest temperature (1,196°F. average or 1,208°F. maximum) and lowest space velocity (0.25) that were used. The greatest conversion of feedstock, 88.1 weight percent, and greatest yield of methane as percent of conversion, 63.3 percent, also were obtained at these conditions. Methane content of the gas was 75.8 volume percent, or 49.7 percent of stoichiometric. Heating value of the gas was 1,202 Btu per cubic foot.

TABLE 2. - Gasification of crude shale oil over depleted uranium catalyst

(average) (maximum) nsumed ne e e e e ene	°F. °F. scf/bb1 scf/bb1 scf/bb1 scf/bb1 scf/bb1 scf/bb1	880 906 906 365 200 146 18	954 979 1840 598 387 247	1010 1035 3080 1152 693 441 29	1053 1074 3980 1507 971 536 18	1102 1125 4170 1767 1059 459
(maximum) nsumed ne e e e e e ne ene	°F. scf/bbl scf/bbl scf/bbl scf/bbl scf/bbl scf/bbl	906 1340 365 200 146 18	979 1840 598 387 247 4	1035 3080 1152 693 441 29	1074 3980 1507 971 536 18	1125 4170 1767 1059 459
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ne	<pre>scf/bbl scf/bbl scf/bbl scf/bbl scf/bbl</pre>	365 200 146 18	598 387 247 4	1152 693 441 29	1507 971 536 18	1767' 1059 459 18
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Ф	scf/bbl scf/bbl	18 33	4 C	. 29	18 40	18
е	scf/bbl	ယ	>	/. /.	04	
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Total	scf/bbl	762	1236	2359	3072	3303
value, gross	Btu/cu.ft.	1589	1570	1565	1550	1481
C ₄ + liquid	wt. %	76.4	67.5	44.9	32.9	30.6
٠.	wt. %	23.6	32.5	55.1	67.1	69.4
eposit	wt. %	5.1	4.7	4.9	4.0	5.5
	wt. %	2.0	2.0	2.0	2.0	2.0
gen sulfide	wt. %	0.6	0.7	0.7	0.7	0.7
	wt. %	1.6	2.0	2.1	2.5	2.4
Methane	wt. %	4.7	7.7	14.8	19.3	22.6
	wt. % of conv.	19.9	23.7	26.9	28.8	32.6
		47.9	48.4	48.8	49.0	53.5
		4.2	6.8	13.2	17.2	20.2

TABLE 3. - Gasification of crude shale oil over cobalt molybdate catalyst

(Pressure 1,000 p.s.i.g.; hydrogen feed 12,000 scf/bbl)

Space velocity			1.0 V	o/V _c /hr.	
Temp. (avg.)	°F.	974	1004	1106	1183
Temp. (max.)	°F.	1018	1049	1172	1226
H ₂ consumed	scf/bbl	2680	3210	48 50	5980
Methane	scf/bbl	652	972	1945	3090
Ethane	scf/bbl	427	663	1292	1699
Propane	scf/bbl	288	435	504 .	109
Ethylene	scf/bbl	27	48	5	0
Propylene	scf/bbl	30 .	57	0	. 5
Total	scf/bbl	1424	2175	3746	4903
Heat value, gross	Btu/cu.ft.	1601	1611	14 90	1315
C ₄ + liquid	wt. %	65.9	50.5	• 24.9	14.9
Conversion	wt. %	34.1	49.5	75.1	85.1
Catalyst deposit	wt. %	2.4	2.0	2.4	4.2
Water	wt. %	2.0	2.0	2.0	2.0
Hydrogen sulfide	wt. %	0.7	0.7	0.7	0.7
Ammonia	wt. %	2.6	2.6	2.6	2.6
Methane	wt. %	8.4	12.5	25.0	39.7
Methane	wt. % of conv.	24.6	25.3	33.3	46.6
Methane	vol. % of gas	45.8	44.7	51.9	63.0
Methane	vol. % of stoich.	7.5	11.1	22.2	35.4

Conditions used with the cobalt molybdate were not generally the same as those used with the depleted uranium catalyst. However, the gas yields obtained at 1,062°F, and 0.50 space velocity over cobalt molybdate were similar to those obtained at 1,053°F, and 0.50 space velocity over depleted uranium. Better elimination of nitrogen from the liquid products was achieved with the cobalt molybdate, as shown by the higher yield of ammonia obtained. No special advantages were found for the depleted uranium, but further research would be needed to fully evaluate it over the entire range of conditions investigated with the cobalt molybdate.

SUMMARY

Cobalt molybdate on alumina and depleted uranium on alumina were tested as catalysts for hydrogasifying crude shale oil at 1,000 pounds pressure with a hydrogen feed rate of 1.1 times the stoichiometric, with on-stream periods of 6 hours for each experiment. Temperatures used were in the range 880° to 1,102°F. with depleted uranium and 974° to 1,196°F. with cobalt molybdate. With both catalysts, the higher reaction temperatures produced greater gas yields, greater percentages of methane in the gas, and greater methane yields expressed as percentage of conversion of feedstock. The high heating values of the gases decreased at the higher reaction temperatures and more nearly approached that of methane. Lowering the space velocity through the range 1.0 to 0.25 with cobalt molybdate produced effects similar to those obtained when raising the temperature. Further research would be necessary to adequately evaluate the process variables when using depleted uranium catalyst.

pressure regulator (P). The unit pressure is indicated by a precision pressure gage, the pressure drop across the catalyst bed by a differential pressure gage. The reactor temperatures and the feed-vaporizer temperatures are controlled by a six-point potentiometric-type on-off temperature controller.

The reactor used in the first series of tests with n-hexane, n-octane, and kerosene was simpler in construction than that used in the remainder of the test program. The major reactor and furnace dimensions are shown schematically in Fig. 2. The reactor had been designed and used for operation at high temperatures and pressures and is described fully elsewhere. Because of its large diameter, the reactor was provided with a thick insert to reduce the internal diameter as well as to contain the catalyst and provide for complete and easy catalyst removal. The entire reactor was heated by a single-zoned electric furnace. The temperatures within the reactor were measured by a single traveling thermocouple made of Chromel-Alumel and insulated with magnesium oxide. It has a 0.040-inch-OD swaged stainless steel sheath. The thermocouple was mounted within an 1/8-inch-OD stainless steel thermowell which was mounted in the top cover of the reactor. Feed vapors entered the top of the reactor, flowed downward through the catalyst bed, and returned to the top of the reactor through a 3/16-inch-OD dip tube sealed into the top cover of the reactor by a compression-type fitting.

The major reactor and electric furnace dimensions for the second reactor are shown schematically in Fig. 3. The furnace has four heating zones; two are on the catalyst bed which is supported and contained by two beds of alumina inerts. Two separate heaters were used in the catalyst zone to provide better temperature control. A thermocouple rake assembly, which contained seven Chromel-Alumel thermocouples was used to measure reactor temperatures. The thermocouples are insulated with magnesium oxide and have 0.025-inch-OD swaged stainless steel sheaths. To minimize possible temperature-measurement errors due to axial heat conduction along the thermocouples assembly, each thermocouple extends perpendicularly from the axial thermowell. To follow the progress of the reaction through the catalyst bed and the deactivation of the catalyst with time, four sampling probes were inserted at the same levels as thermocouples 3, 4, 5, and 6. The probes were located approximately 1/4 inch, 1-1/2 inches, 2-3/4 inches, and 4 inches below the top of the bed.

Methods were developed for collecting and analyzing the gas and liquid samples taken with the probes. These methods allow continuous samples to be withdrawn simultaneously at all four points within the catalyst bed. The bed ranged from 25 to 200 cc in volume. Since the total flow rate of the probe samples is only a few percent of the total exit stream flow rate, the stability of reactor operation is not impaired, and the flow rate in the bed does not vary appreciably. A Precision Scientific Co. Chronofrac gas chromatograph was installed for analyzing probe and product gas samples.

A special feed system was devised for high-vapor-pressure light hydrocarbons such as propane and butane. The light hydrocarbons were fed through a high-pressure rotameter from pressurized stainless steel cylinders. Two cylinders were used so that one cylinder could be used to feed the hydrocarbon while the other was being weighed. The cylinders were switched and weighed at the beginning and end of each steady-state period so that the hydrocarbon feed rate; could be

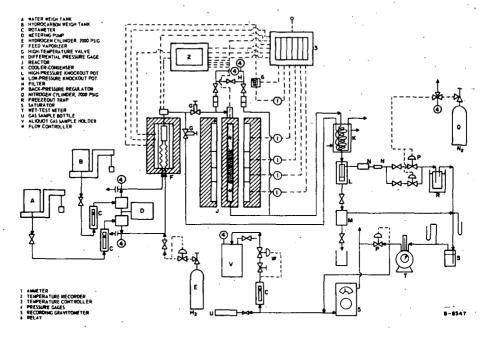
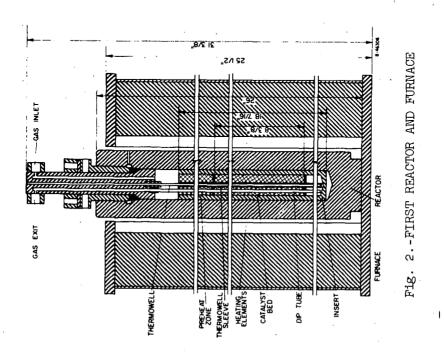


Fig. 1.-CATALYST TESTING UNIT



measured more accurately. The tanks were provided with quick-disconnect couplings at each end. These couplings contained double, integral chedk valves to reduce loss of hydrocarbon during the switching operation to a minimum.

Feedstocks were obtained from several sources. Pure hydrocarbons were obtained from Phillips Petroleum Company. The n-hexane and benzene were pure grade (99.0 mole percent minimum purity). The n-octane was technical grade (95.0 mole percent minimum purity).

The propane used was a commercially available feed supplied by Pyrofax Corporation. The light kerosene, supplied by Universal Oil Products Company, had been partially desulfurized. The light fuel naphtha was obtained from Industrial Solvents Corporation. The jet fuel was obtained from Humble Oil and Refining Company. The properties of the commercial feeds are presented in Table 1.

Chemical and physical analyses of liquid feeds were performed by A.S.T.M. standard methods where applicable. Gaseous feeds and product gases were analyzed by a method which is based largely on that given by Hoggan and Battles and Bertolacini and Barney. The liquid feeds, having low sulfur contents, were analyzed for sulfur by a method given by Attari.

RESULTS

Thermodynamic Equilibrium Studies

A detailed thermodynamic equilibrium study was made for a number of pure hydrocarbon feedstocks to calculate the effects of operating variables on the heat of reaction and product gas composition. These calculations were made because experimental work done elsewhere had shown that product gas compositions approached equilibrium quite closely with active catalysts. It was thus expected that not only would these calculations be a guide for conducting experimental work, but also would minimize the amount of experimental work required.

Equilibrium gas compositions, heats of reaction, and adiabatic temperature changes were calculated for each initial reaction temperature. The variables studied were temperature, pressure, feed steam/carbon ratio, and feedstock.

Equilibrium gas compositions (on a dry basis) for steam reforming of n-hexane are given as a function of temperature, pressure, and feed steam/carbon ratio in Fig. 4. In the range of variables studied, the carbon dioxide content is almost independent of temperature, pressure, and feed steam/carbon ratio above a pressure of 10 atm and below 750°K. The carbon monoxide content is affected by temperature and pressure, but is not present in substantial concentrations. Increasing the pressure and decreasing the temperature results in increases in raw gas heating value, since methane content increases and hydrogen content decreases. The high hydrogen contents shown at 1 atm, 800°K, and high steam/carbon ratios suggest the possibility of using this process for hydrogen production in some systems, such as fuel cells, where a pure hydrogen stream is not required.

The effect of paraffin carbon number on the equilibrium methane concentration is shown for three feed steam/carbon ratios in Fig. 5. These results indicate that a higher methane content gas can

Table 1.-COMMERCIAL FEEDSTOCK PROPERTIES

	COMMERCIAL FE	EDSTOCK PROPER!	PIES
Liquid Feeds	Light		Light
Feedstock	Naphtha	Jet Fuel	Kerosene
Source	Industrial Solvents Corp.	Humble Oil & Refining Co.	Universal Oil Products Co.
Specific Gravity, OAPI (60°/60°)	70.3	56.5	48.8
ASTM Distillation, I.B.P. 5% 10% 20% 30% 40% 50% 60% 70% 80% 90% End Point Recovery, % Residue, % Ultimate Analysis, Carbon Hydrogen Total C/H Ratio	167 171 173 174 176 176 180 183 187 194 203	194 238 258 268 293 302 303 303 479 479 84.56 995.85	361 371 3778 384 388 394 408 416 430 445 98 2 85.41 14.50 50 50 50
Sulfur, ppm Hydrocarbon Type A Analysis, vol % Aromatics Olefins Saturates Total	2.0 0.0 98.0 100.0	10.6 4.6 84.8 100.0	5.3 1.1 . <u>93.6</u> 100.0
Gaseous Feed	•		
Feedstock	Propane	•	
Source	Pyrofax Corp.		
Composition, mole propane Propale Propylene Ethane i-Butane n-Butane Total	94.5 2.5 1.5 1.0 0.5 100.0		
Sulfur Content, pp	m 16.8		•

TABLE 4. - Gasification of crude shale oil over cobalt molybdate catalyst

(Pressure	1.000	D. S. i . g	hydrogen	feed	12 000	scf/hhl

Space velocity		$0.50 \text{ V}_{\text{O}}/\text{V}_{\text{C}}/\text{hr}$.		0.25 $V_o/V_c/hr$.	
Temp. (avg.)	°F.	1062	1114	1106	1196
Temp. (max.)	°F.	1089	1141	1129	1208
H ₂ consumed	scf/bbl	3803	4985	5460	6852
Methane	scf/bbl	1465	2141	2485	4341
Ethane	scf/bbl	995	1379	1683	1357
Рторапе	scf/bbl	461	407	231	25
Ethylene	scf/bbl	9	23	0	1
Propylene	scf/bbl	24	18	18	1
Total	scf/bbl	2954	3968	4417	5725
Heat value, gross	Btu/cu.ft.	1530	1451	1393	1202
C4+ liquid	wt. %	35.5	23.2	20.2	11.9
Conversion	wt. %	64.5	76.8	79.8	88.1
Catalyst deposit	wt. %	4.7	2.6	1.4	4.1
Water	wt. %	2.0	2.0	2.0	2.0
Hydrogen sulfide	wt. %	0.7	0.7	0.7	0.7
Ammonia	wt. %	2.6	2.6	2.6	2.6
Methane	wt. %	18.8	27.5	31.9	55.8
Methane	wt. % of conv.	29.1	35.8	40.0	63.3
Methane	vol. % of gas	49.6	54.0	56.2	75.8
Methane	vol. % of stoich.	16.8	24.5	28.4	49.7

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